
A Surface Analytical Examination of Stringer Particles in Al-Li-Cu Alloys

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A SURFACE-ANALYTICAL EXAMINATION OF STRINGER PARTICLES

IN ALUMINUM-LITHIUM-COPPER ALLOYS

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A surface-analytical examination of powder-metallurgy processed Al-Li-Cu alloys was conducted. The purpose of the work was to characterize the oxide stringer particles often found in these alloys. Particle characterization is important to a better understanding of the effect of the particles on the stress-corrosion and fracture properties of the alloy. The techniques used were secondary ion mass spectroscopy and scanning Auger microscopy. The results indicate that the oxide stringer particles contain both aluminum and lithium, with relatively high lithium content, and that lithium compounds may be associated with the stringer particles, thereby locally depleting the adjacent matrix of lithium solute.

Introduction

Aluminum-lithium alloys are the subject of considerable research because they can exhibit a substantial specific-strength and specific-stiffness advantage over the presently available commercial 2000- and 7000-series aluminum alloys (see, for example, Ref. 1). One such effort is an attempt to improve the ductility of these alloys through the use of powder-metallurgy (P/M) techniques in order to obtain a more uniform and refined microstructure. However, like the commercial high-strength aluminum alloys, these new P/M aluminum-lithium alloys may be susceptible to stress corrosion in a chloride-containing aqueous environment. A research objective at Ames Research Center is to evaluate the stress-corrosion behavior of selected P/M processed aluminum-lithium alloys.

The results of a stress-corrosion study of P/M Al-Li-Cu alloys are reported in a companion paper for this conference (2). A major result of that study is the correlation of microstructural features to pitting and subsequent crack initiation. These microstructural features were primarily oxide particles that are strung out along the extrusion direction during consolidation and processing of the alloys. In order to more fully understand the chemical and microstructural properties of these alloys, and in particular the role of the stringer oxide particles in affecting these properties, studies were undertaken to examine the alloys by transmission electron microscopy (TEM) (3) and by surface-analytical techniques. This paper is a preliminary report of the surface-analytical investigation.

The surface-analytical methods used were secondary-ion mass spectroscopy (SIMS) and scanning Auger microscopy (SAM). These techniques were chosen because they are sensitive to low-mass elements (in particular lithium), and because correlated data on the elemental compositions of the alloys may be obtained. SIMS is sensitive to trace levels for all elements and, in addition, the SIMS apparatus used in this investigation can image these elements at a spatial resolution of approximately 5 μm . SAM has a detection limit of about one atomic percent; however, the elemental composition can be imaged to a 60-nm resolution.

Experimental

The nominal compositions of the alloys used in this study are

- 1) 2.6 wt % lithium and 1.4 wt % copper with the remainder aluminum, and
- 2) the same lithium and copper contents with 1.6 wt % magnesium. Both alloys contain about 0.1 wt % zirconium for microstructural stability.

Electro-thinned specimens, suitable for thin-film TEM, were employed in the surface-analytical studies. Thin specimens were prepared by spark-cutting 3-mm diameter disks from 0.25-mm-thick foils obtained from flat coupons used in a tensile-properties characterization study (4). The initial thickness of the tensile coupons was 1.5 mm. The 0.25-mm-thick foil from the undeformed grip section was prepared using standard metallographic polishing techniques to remove material equally from both surfaces. Final electro-polishing was done using the twin-jet technique in a 70-30% (by volume) methanol-nitric acid electrolyte at -20°C and at a current density of 0.2 A/cm^2 . These conditions correspond to the polishing region in the current-versus-voltage polarization curve. The samples examined by SIMS were the magnesium-bearing alloy; the sample examined by SAM was the base alloy. Details of the material processing treatment have been reported previously (2,4).

Secondary ion mass spectroscopy (SIMS) is a technique in which a directed ion beam is used to sputter successive layers of material from the surface of a sample. Because SIMS is an ion-bombardment technique, cleaning of the surface is accomplished in the initial phases of experimentation. A portion of the sputtered material will be in the form of atomic and molecular ions. After collection and mass separation, these ions are detected to obtain elemental information. The detection limit for a given element depends on the ionization potential or electron affinity and the presence of any interfering species, but can extend into the parts-per-billion range for many elements. The instrument used in this study was a CAMECA IMS-3F secondary-ion microscope. In addition to standard SIMS spectra, secondary-ion images were displayed for viewing on a fluorescent screen.

Scanning Auger microscopy, based on Auger electron spectroscopy, is a technique in which an electron beam is used to probe the sample surface. A portion of the resulting secondary electrons are element-specific and originate in the first few atomic layers. The scanning Auger microprobe consists of a standard ultrahigh-vacuum work chamber in which a base pressure of 30 nPa is achieved, and a 6-in. cylindrical mirror analyzer with an integral field-emission-electron source. Under normal operating conditions, the electron source gives a 5-nA electron beam at a primary energy of 5 keV. The spatial resolution of this source has been shown to be 30 nm (5). The system includes a sample introduction chamber and facilities for argon-ion sputtering of the samples. Prior to SAM examination, the sample used in this investigation was cleaned by argon-ion bombardment until metallic aluminum was observed. The microprobe is operated under computer control to obtain Auger spectra in either EN(E) or EdN(E)/dE modes and elemental images of the sample surface.

Results

Secondary-Ion Mass Spectroscopy

Two SIMS experiments were performed on clean specimen surfaces: 1) a depth-profile experiment to determine the relative change in composition as a function of depth into the specimen and 2) imaging experiments to determine the spatial distribution of the elements. The depth-profile experiment revealed the distribution of major elements to be relatively constant to a depth of about 3 μm . Additionally, several trace elements were observed, including hydrogen, boron, silicon, phosphorus, sulfur, and chlorine. These elements are probably present in parts-per-million concentrations since the magnitudes of their SIMS peaks were at least a factor of 100 smaller than those of the major elements. Zirconium, added to both alloys as a grain stabilizer, was also detected in the SIMS experiments.

Typical results of SIMS elemental imaging experiments are shown in Figure 1 for oxygen primary-ion bombardment and in Figure 2 for cesium primary-ion bombardment. Oxygen-ion bombardment enhances the production of positive secondary ions from the surface; aluminum, lithium, magnesium, and zirconium images are presented in Figure 1. Cesium-ion bombardment enhances the production of elements with high electron affinities; SIMS elemental images for aluminum, oxygen, carbon, and lithium are shown in Figure 2. As can be seen, the bright areas in these figures (indicating the location of the specific element) form rows or streaks across the field of view. The streaks of the oxygen image (Fig. 2b) show a high degree of correlation with the stringer particles that are observed in these alloys (2) and are shown in the scanning electron image of Figure 3. Likewise, the lithium images (Figs. 1b and 2c) correlate well with the stringer particles. The magnesium image of Figure 1c correlates well with the stringer particles but does not

correlate 1:1 to the respective lithium image (Fig. 1b). The aluminum images (Figs. 1a and 2a) correlate inversely with the stringer particles, the matrix between the stringers being bright and the stringers being dark. The lesser elements identified above in the depth-profile experiment showed no significant correlation with the stringer particles. Therefore, the stringer particles appear to be primarily lithium oxide. The zirconium image (Fig. 1d) is banded, indicating an inhomogeneous distribution of the element. These bands are parallel to the extrusion direction of the alloy, but do not necessarily correlate with the stringer particles.

Scanning Auger Microscopy

Scanning-electron micrographs of the Al-Li-Cu specimen surface taken with the SAM instrument are shown in Figure 3. The image shown in Figure 3a was taken at a primary voltage of 5 keV; the image in Figure 3b was taken at a primary voltage of 2.5 keV. The contrast difference between the two images shows a clear difference between the bright matrix and the relatively dark areas surrounding the oxide stringer particles. The particles themselves are very bright, a result of the charging of a nonconducting oxide. This charging effect made Auger spectra of the particles unreliable, and only a few spectra could be obtained from the particles that maintained a uniform charge with time. Attention was focused on the stringer particles and the dark areas adjacent to the particles (Fig. 3b).

Comparative Auger spectra of the alloy matrix and the dark areas adjacent to the oxide stringer particles (Fig. 3b) are shown in Figure 4. These are low-energy spectra, with negative Auger signal excursions anticipated at 43 eV and 34 eV (lithium), at 68 eV (metallic aluminum), and at 51 eV and 35 eV (aluminum oxide). As can be seen from the figure, the specimen matrix is composed almost entirely of aluminum, with minor indications of aluminum oxide and possibly lithium. The poor energy resolution of the metallic aluminum indicated in this spectrum is most probably the result of an aluminum oxide excursion at 51 eV and possibly a copper excursion at 60 eV.

The region adjacent to the stringer particles is seen in Figure 4 to be rich in lithium, depleted in metallic aluminum, and to contain some aluminum oxide. Using standard spectra from the literature (6), a semiquantitative analysis indicates an Li:Al ratio of about 3:2, although this estimate could be in error by as much as 25%.

As mentioned above, the stringer particles themselves were difficult to examine because of charging effects. Spectra that were shifted in energy were obtained in those cases in which the particles would charge uniformly. These spectra indicate that the stringer particles are an oxide, substantially similar in composition to the surrounding lithium-rich region (Fig. 4) with an approximate Li:Al ratio of 3:2.

SAM elemental images for aluminum, lithium, and carbon are shown in Fig. 5. The image of metallic aluminum (Fig. 5a) is generally bright, with dark strips running horizontally where the stringer particles are located. The lithium image (Fig. 5b) shows regions of relatively high lithium content that correlate well with the stringer particles. Oddly enough, the carbon image (Fig. 5c) indicates the association of carbon with the lithium-rich areas. The contrast variations exhibited in the SAM elemental images are a direct function of the signal-to-noise ratio for the respective element, and this ratio is a function of the ability of the element to produce Auger emission under a given electron-beam intensity, as well as a function of the concentration of the element present. The contrast differences between the lithium and carbon images of Figures 5b and 5c, respectively, are more

indicative of the low Auger signal for lithium with respect to carbon than they are of actual variation in concentration.

The relatively high carbon content observed in the region of the stringer particles is very unusual for argon-ion-cleaned material, which suggests that the carbon may be present in the bulk of the material and not a surface effect. Additional Auger samples were prepared by reactive oxygen-ion sputtering followed by argon-ion cleaning. Oxygen sputtering tends to oxidize the surface and will preferentially remove surface carbon layers. A surface layer of the order of 10 nm was removed in this process, which is generally sufficient to remove contamination. However, analysis showed essentially carbon distribution equivalent to that observed for argon-ion cleaning alone (Fig. 4c). In these regions, the carbon content is estimated to be as high as 40 atomic percent.

Discussion

The preliminary data presented here strongly suggest that high lithium content phases or compounds are associated with the oxide stringer particles found in powder metallurgically processed Al-Li-Cu alloys or that the oxide particles themselves are lithium rich or both.

The SIMS results show a correlation of the oxide stringer particles with the lithium distribution and a lack of correlation with the trace elements hydrogen, boron, silicon, sulfur, phosphorus, and chlorine. The SAM results show conclusively that the lithium is in fact segregated in areas surrounding the stringer particles. The resulting lithium-rich areas are of interest in understanding the stress-corrosion properties of the subject alloys (2). In a semiquantitative manner, the Al:Li ratio in these enriched areas was determined to be 2:3. An examination of aluminum-lithium or pure lithium standards is necessary to provide comprehensive quantitative analysis; it will be performed at a later date.

An unresolved experimental question of this study is the unusual carbon levels observed to be associated with the stringer particles (Fig. 5c). Carbon may be introduced at some stage of processing — atomization, consolidation, processing, or heat treatment — of the powder-metallurgy processed Al-Li-Cu alloys. Studies will continue in an attempt to resolve this question.

A number of discrepancies exist between the surface-analytical results reported here and the microstructural results reported in a companion paper (3). Specifically, TEM bright-field examination coupled with selected area diffraction and microdiffraction of the regions adjacent to the stringer particles did not indicate the presence of a large-scale lithium-containing phase. However, a difference in electron scattering intensity was observed between these regions and the matrix. This was taken as evidence suggesting the presence of some elemental species in a supersaturated state rather than in a separate crystallographic form. The results of our surface analysis suggest that lithium is the elemental species.

From the TEM studies, a fine and uniform distribution of δ' -phase (Al_3Li) was identified in the alloy matrix (3). In contrast, our surface-analytical results did not clearly show lithium in the alloy matrix. It must be reasoned, then, that the distribution of δ' particles in the matrix must not be sufficient to produce a detectable signal using SAM.

Finally, TEM results indicate the presence of small companion particles adjacent to the oxide stringers (3). These particles appear to exhibit a

crystalline structure. From the surface-analytical results, it is suggested that these particles may be a lithium-rich phase, such as Li_2O ; δ' -phase (AlLi); Al_4Li_3 ; AlLi_2 ; Al_5CuLi_3 ; or Li_2CO_3 . Work is continuing to identify this phase.

Conclusions

The results of this preliminary surface-analytical investigation show that lithium segregates in P/M Al-Li-Cu alloys. This segregation is in rows of oxide stringer particles and shows two distinct forms. The first form is the stringer particles themselves, which appear to be a lithium-aluminum oxide with an Li:Al ratio of about 3:2. The second form is in the regions surrounding the stringer particles; these regions show the same Li:Al ratio of 3:2 but appear to contain significant carbon.

Several other elements were observed in the surface-analysis experiments, in particular, hydrogen, boron, silicon, sulfur, phosphorus, and chlorine. However, these elements are present in very low concentration and do not correlate with the stringer oxide particles.

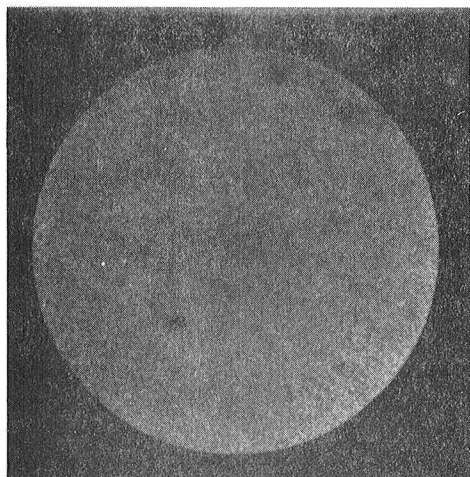
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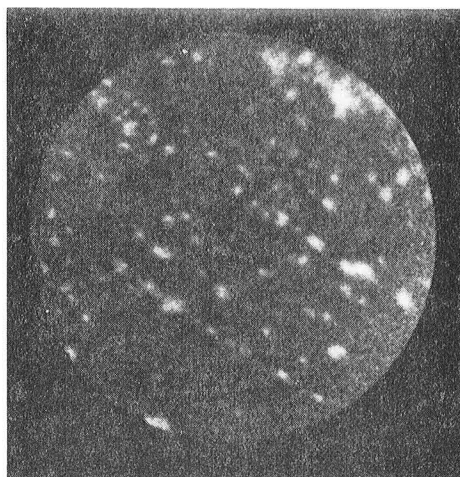
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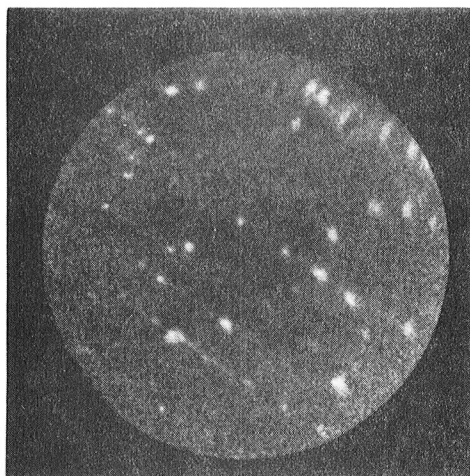
(a) ALUMINUM



(b) LITHIUM



(c) MAGNESIUM



(d) ZIRCONIUM

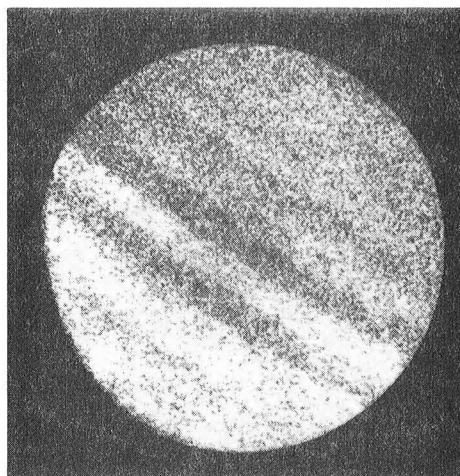
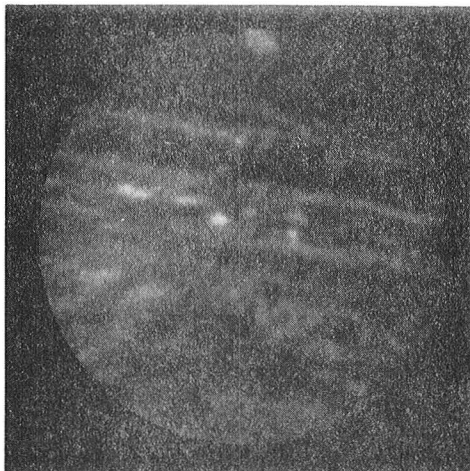
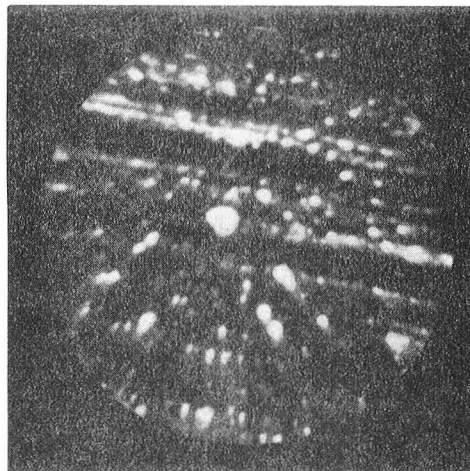


Figure 1 - SIMS elemental images of the magnesium-bearing alloy using oxygen primary ion bombardment. (a) Aluminum image; (b) lithium image; (c) magnesium image; (d) zirconium image.

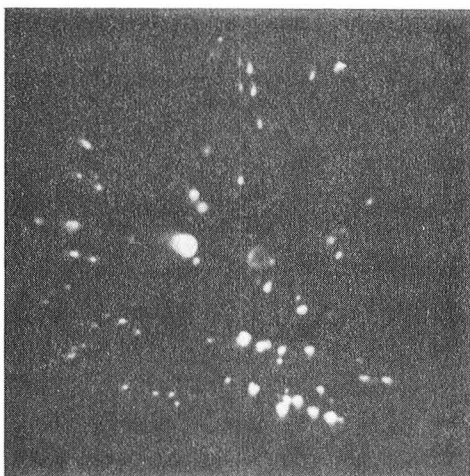
a) ALUMINUM



b) OXYGEN



c) CARBON



d) LITHIUM

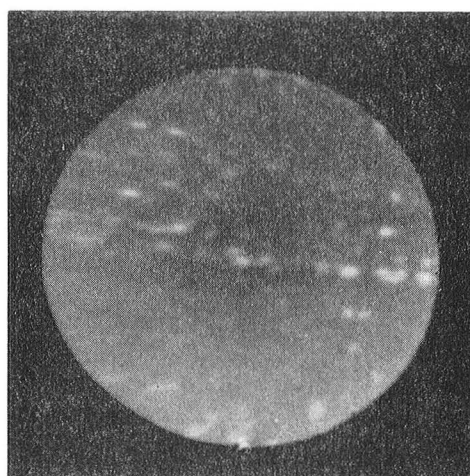
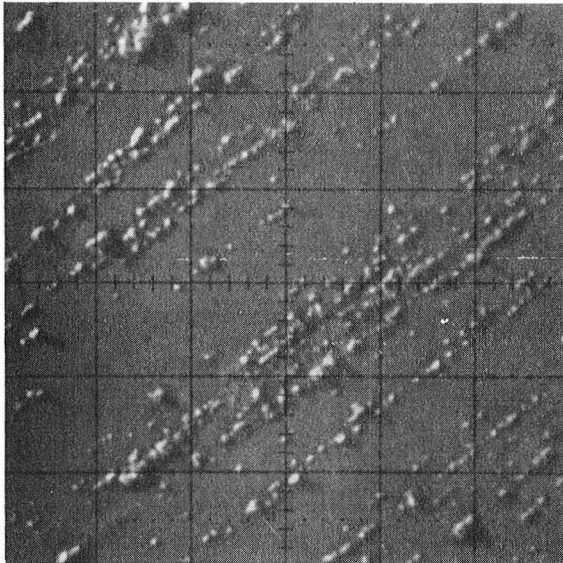
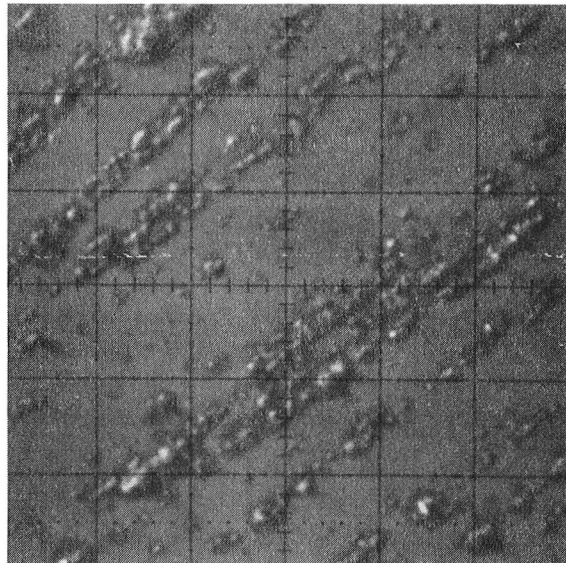


Figure 2 - SIMS elemental images of the magnesium-bearing alloy using cesium primary ion bombardment. (a) Aluminum image; (b) oxygen image; (c) carbon image; (d) lithium image.

a) 5 keV PRIMARY



b) 2.5 keV PRIMARY



←→ 15 μm

Figure 3 - SEM images of the stringer particles in the alloy surface illustrating contrast near the particles. (a) At 5 keV; (b) at 2.5 keV.

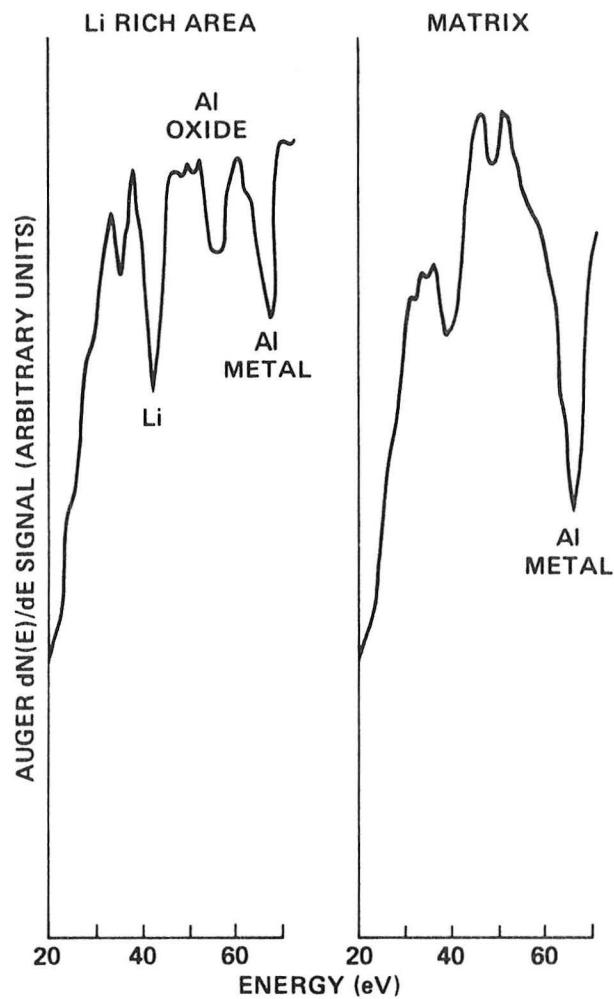
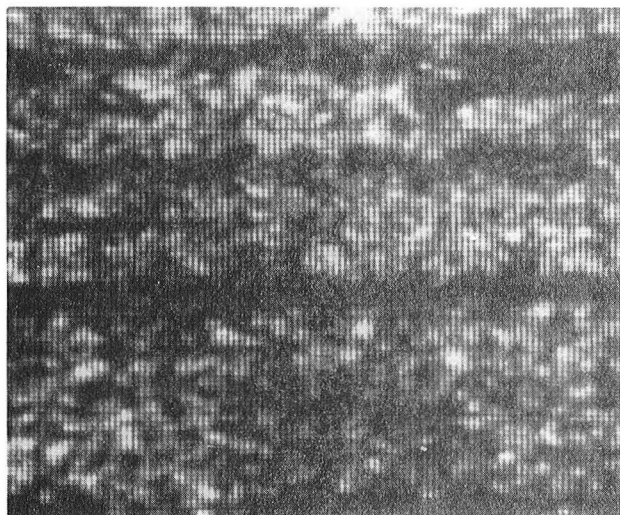
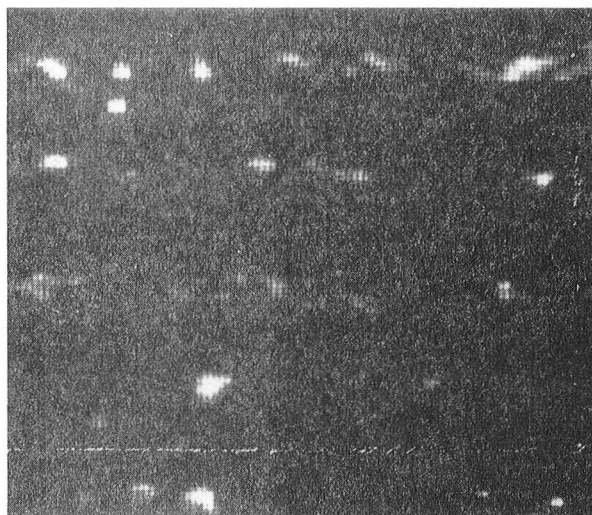


Figure 4 - Low energy Auger spectra of the matrix and Li-rich metal.

a) ALUMINUM METAL



b) LITHIUM



c) CARBON

↔
10 μm

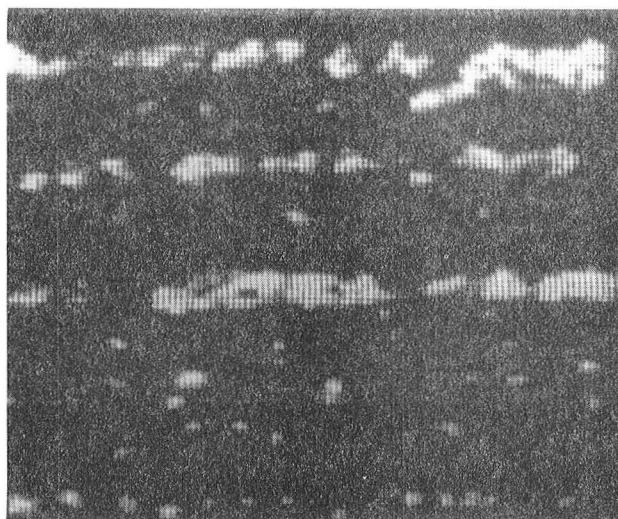


Figure 5 - SAM elemental images of the oxide stringers. (a) Metallic aluminum image; (b) lithium image; (c) carbon image.

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16. Abstract A surface analytical examination of powder metallurgy processed Al-Li-Cu alloys has been conducted. The particular focus of this work is to characterize the oxide stringer particles often found in these alloys. Particle characterization is important to more fully understand their impact on the stress corrosion and fracture properties of the alloy. The techniques used were SIMS (Secondary Ion Mass Spectroscopy) and SAM (Scanning Auger Microscopy): The results indicate that the oxide stringer particles contain both Al and Li with relatively high Li content and the Li compounds may be associated with the stringer particles, thereby locally depleting the adjacent matrix of Li solute.			
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